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13. ABSTRACT *(Maximum 200 words)*

Thermoelectric materials use temperature differences to produce electricity or use electrical power to produce cooling. The first property is used in energy recovery from hot gases (e.g. to make electricity from exhaust gases coming out of engines). The second is used to make refrigerators that have no moving parts, cause no pollution, and can cool microelectronic systems. Both types of devices are currently used only for special applications, since they are not economically competitive. However, they would be if some of their properties could be improved by a factor of two or more. In our work we use theory to anticipate which compounds, in a class of candidates called semiconductor clathrates, are likely to have superior thermoelectric properties. Such predictions help the experimentalists to focus on the synthesis and characterization of the most promising candidates.

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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: **N00014-96-1-0054**

PR Number **97PR00275-00**

Electronic and Optical Properties of Doped Zeolites and Clathrates: Display and Thermoelectric Applications

Horia Metiu

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August 10, 1998

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
FOR THE PERIOD 6/1/97-5/31/98

PR Number: 97PR00275-00

Contract/Grant Number: N00014-96-1-0054

Contract/Grant Title: Electronic and Optical Properties of Doped Zeolites and Clathrates

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a. Number of papers submitted to refereed journals, but not published: 3

b. Number of papers published in refereed journals: 2

c. Number of books or chapters submitted, but not yet published: 2

d. Number of books or chapters published: 1

e. Number of printed technical reports/non-refereed papers: 0

f. Number of patents filed: 0

g. Number of patents granted: 0

h. Number of invited presentations: 7

i. Number of submitted presentations: 0

j. Honors/Awards/Prizes for contract/grant employees: 0

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 2

Graduate Students: 0

Post-Doctoral Associates: 2

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

the number of

Minority* Graduate Students: 0

Minority* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

l. Other funding

PART I

a. Papers submitted to refereed journals, but not published
b. Papers published in refereed journals
c. Chapters submitted, but not yet published
d. Chapters published

1. Self-Interaction-Corrected Band Structure Calculations for Intracavity Electrons in Electro-Sodalite, N. P. Blake and H. Metiu, *J. Chem. Phys.*, submitted

2. Electron Traps and Polaron Formation in Dehydrated Sodalite, N. P. Blake, P. C. Weakliem, and H. Metiu, *J. Chem. Phys.*, submitted

3. An *Ab-Initio*-Based Transferable Potential for Sodalites, N. P. Blake, P. C. Weakliem, and H. Metiu, *J. Phys. Chem.*, to appear

4. Fitting Potential Energy Surfaces: A Search in the Function Space by Directed Genetic Programming, D. E. Makarov and H. Metiu, *J. Chem. Phys. 108*, 590 (1998)

5. Electrons Solvated in Zeolites, N. P. Blake and H. Metiu, *Proc. Australian Summer School on Condensed Matter Physics* (January 1997), M. K. Das, editor, World Scientific, Singapore (1998)

6. Migration of Hydrogen on a Solid Surface: The Physics of the Process and the Methodology, H. Metiu, *Proc. Fermi School on the Dynamics of Rare Events* (Lerici, July 1997)

7. The Rate of Photon Absorption, H. Metiu, *Proc. Fermi School on the Dynamics of Rare Events* (Lerici, July 1997)

8. Some Constraints Involving the Statistical Properties of Trajectories Run in the Monte Carlo Computation of a Rate Constant and Their Use in Improving and Testing the Quality of Sampling, D. E. Makarov and H. Metiu, *J. Chem. Phys. 108*, 8155 (1998)

h. Invited presentations

Searching for Potentials and Bootstrapping Times Scales, UCSB Institute of Theoretical Physics Workshop on Interatomic Potentials and Linking of Scales, June 5-7, 1997

Activated Dynamics on Surfaces, Euroconference on Technical Advances in Particle-Based Computational Material Sciences "Computer Simulation of Rare Events and the Dynamics of Classical and Quantum Condensed Phase Systems", Lerici, Italy, July 7-18, 1997

Genetic Programming in Quantum Mechanics, Symposium on Time Propagation Methods, Fifth Chemical Congress of North America, Cancun, November 11-15, 1997

Coherent Processes in Quantum Wells, Symposium on Laser Control of Electrons and Molecules, Fifth Chemical Congress of North America, Cancun, November 11-15

Island Shapes, Evaporation, and Migration, 18th IUVSTA Workshop "Diffusion and Growth in Ultrathin Layers", Newcastle (Australia), November 17-21, 1997 (presented by Shudun Liu)

Coarsening of an Ensemble of Islands on a Solid Surface, University of Pennsylvania, February 12

Coarsening of an Ensemble of Islands on a Solid Surface, Symposium on Mechanisms and Principles of Epitaxial Growth in Metallic Systems, Materials Research Society Meeting, San Francisco, April 13-17

l. Other funding

There is no relationship between the work supported by this grant and the following:

National Science Foundation Chemistry Division "Theoretical Studies in Quantum Dynamics" 8/1/94-7/31/98, $365,000 total

Air Force Office of Scientific Research"Computer Simulation of Growth Phenomena" 11/1/94-10/31/97, $303,500 total

National Science Foundation "Center for Quantized Electronic Structures (QUEST)", 1993-98 (one of 17 co-PIs)

PART II

a. Principal Investigator: Horia Metiu

b. Current telephone number: (805) 893-2256

c. Cognizant ONR Program Officer: John C. Pazik

d. Program objective

We use theoretical methods to help Prof. Galen Stucky's group in their search for better thermoelectric materials. We examine a class of compounds based on Si, Ge, or Sn which have a clathrate structures. There are about 100 such compounds, each allowing a fair number of chemical variations (doping, slightly non-stoechiometric composition, etc). They are difficult to synthesize and characterize structurally and the measurements of their transport properties are very tedious. For this reason it would be extremely useful to provide theoretical guidance and develop methodology that will allow us to determine, before synthesis, which among these compounds is likely to have the best thermoelectric properties. We are providing such guidance by performing density functional calculations of the band structure of these compounds and using it to estimate the Seebeck coefficient and the electrical conductivity. These calculations, though difficult, are more rapid than experimental synthesis and characterization. Our work will allow the experimentalists to focus on the more hopeful candidates. We are also proposing the synthesis of new clathrates based on GaAs, AlAs, In As, CdTe and other tetrahedrally bonded compounds. By performing total energy calculations we can determine which among these compounds are stable, as compared to other solids that can be made from the same atoms, and therefore have a good chance of being prepared in the laboratory.

e. Significant results during last year

Our main effort, in collaboration with Prof. Galen Stucky, has been directed towards determining whether zeolites containing one solvated electron in each cage are good thermoelectric materials. For this we had to understand the electronic structure of the material. Calculations that explained most of the measured quantities indicated that the material is a metal with low electron density. However, disagreement with the low-temperature magnetic susceptibility measurements forced us to substantially refine the model. By using density functional calculations, which include generalized gradient and self-interaction corrections, we have shown that the system is an antiferromagnetic Mott insulator.[1] This means that, in spite of the fact that the Seebeck coefficient and thermal conductivity are favorable, this class of new substances will not contain good thermoelectric materials since they will not have sufficient electrical conductivity.[1,2] In this work we have reached a very important conclusion: it is not possible to obtain even a qualitative

understanding of the electronic properties of a narrow-band solid without making the self-interaction correction, which is usually neglected in solid state calculations. Another important achievement is the development of a new method, directed genetic programming,[4] to find potential energy functions that fit the energies calculated by *ab initio* methods. This difficult, tedious, and important problem can now be given to computers.

I was invited to lecture on electrons in zeolites at two summer schools (in Australia[5] and Europe[6,7]) and this gave me a chance to review some of our ONR-sponsored work for a broader audience of physicists and chemists.

The bulk of our work this year has been developing software for calculating the electronic and transport properties of semiconductor clathrates (see item f).

f. Brief summary of plans for next year's work

We are now concentrating on class of clathrate compounds that promise to be excellent thermoelectrics. There are four types of interesting clathrates, described by the formulae A_xT_{136}, A_8T_{48}, $A_8Y_8T_{38}$, and $B_8Y_{16}T_{38}$, where T are tetrahedrally coordinated atoms (Si, Ge, Sn); A are alkali atoms; B are Sr, Ba, Ca; and Y are Al, Ga or In. So far the transport properties of only one compound of each type have been studied experimentally and they all have promising thermoelectric properties. One of them, $Sr_8Ga_{16}Ge_{38}$, has a figure of merit half that of the best commercial compound. There are about 100 clathrates and their transport properties can be changed by chemical modifications. It is extremely likely that some among them are better thermoelectrics than the ones already studied. We plan to use density functional band structure calculations to aid the experimentalists find which clathrates have a chance of being the best thermoelectrics. In these calculations we determine the band structure, and estimate the Seebeck coefficient and the electrical conductivity. We have spent a lot of time developing the software needed for these calculations and have just started performing them. We have found that Si_{48} is a semiconductor with a larger band gap than Si. Na_8Si_{48} is a metal formed because the alkali atoms donate electrons in the conduction band of Si_{48}. The compound $Na_8Al_{23}Si_{23}$ is a metal and it is likely to have a low Seebeck coefficient. Such calculations, while extremely laborious, are faster than the synthesis of compounds and measurements of transport properties and will serve as a guide to pick the promising compounds for synthesis.

g. List of names of graduate students and post-doctoral(s) currently working on the project: Dr. Paul Weakliem, Dr. Nicholas Blake, Dr. Dmitrii Makarov

PART III

Figure 1 (5-part). We show the structure of a clathrate having 48 frame atoms in the unit cell. The frame atoms (e.g. Si or Ge) make cages which are filled with alkali or alkali earth metals.

Figure 2 (on page 2). The sodalite cage consisting of -Si-O-Al-O-Si-O-Al-O-Si- chains. The solid are made by joining the cages at their hexagonal faces. There are four ions and an electron inside each cage.

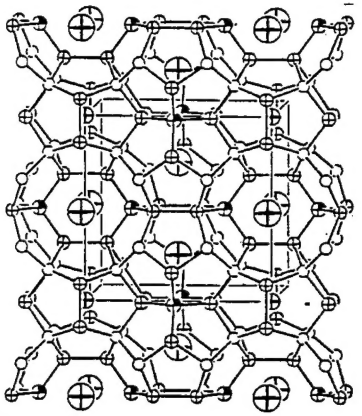
Figure 3. There is no figure 3.

Electronic and Optical Properties of Doped Zeolites and Clathrates

Horia Metiu, University of California, Santa Barbara

Technology Issues: to increase the efficiency of thermoelectric materials for energy recovery and refrigeration

Objectives: to search for better thermoelectrics among the compounds in classes of new materials such as doped zeolites and semiconductor clathrates



Approach:

- use new methodology to find whether doped zeolites can be good thermoelectrics
- use density functional calculations to examine which among the existing clathrates is likely to be a superior thermoelectric
- calculate the properties of hypothetical clathrates to test stability and evaluate thermoelectric properties

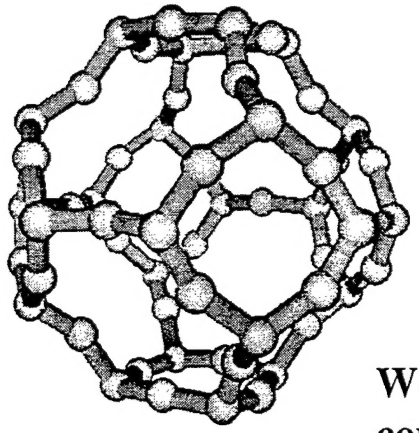
Accomplishments:

- developed a spin density functional method with self interaction correction for solids
- showed that all doped zeolites are Mott insulators
- developed code for using the density functional theory for clathrates and to calculate the Seebeck coefficient and the conductivity

Impact & Transition:

- spin polarized density functional calculations with self interaction corrections must be used to understand the electronic properties of these materials
- all fully doped zeolites are Mott insulators and will not be conducting enough to make good refrigeration devices
- no compound of the type $Na_8Al_{23}Si_{23}$ can be a good thermoelectric

Fully doped zeolites with an electron in each cage



- **Sodalite is made of the cages shown at the left**
- **Each cage is made of -Al-O-Si-0-Al-O-Si- chains.**
- **The cages are joined through the hexagonal windows.**
- **Inside each cage there are four Na ions and electron**
- **The electron is delocalized over the solid**
- **This new material is called electro-sodalite**

We have developed the theory of this type of system to study if such compounds are good thermoelectrics.

Density functional calculations at the highest level performed today predicted that the system is a low density metal. It also predicted a light absorption spectrum and a Knight shift that were very close to the measured one.

The calculations could not explain the low temperature antiferromagnetism

A spin density functional calculation did not lead to the correct result unless we made a self-interaction correction. This correction is neglected in practically all calculations for solids, because of the belief that the delocalization of the electron makes it unnecessary. We have found that without it one cannot obtain the correct antiferromagnetic ground state.

Once the correction is made it changes qualitatively the nature of the material: instead of being a metal it is a Mott insulator. This means that no doped zeolite will have enough electrical conductivity to be a good thermoelectric..

A theoretical study of clathrates

The thermoelectric properties of only four, out of about a hundred clathrates, have been measured experimentally. They are all good thermoelectrics and one ($Sr_8Ga_{16}Ge_{30}$) is close to the best commercially used compound.

The properties of these compounds are very sensitive to chemical modifications (doping, substitution, change of stoicheometry).

We have started to use density functional calculations to assess the likelihood that some of the other compounds in this class are good thermoelectrics.

The clathrates have an extremely large unit cell. Good quality calculations can be performed only with a program which is very fast and is using memory very efficiently.

We have developed several versions of such a program: one running on work stations, two running on an Origin 2000 machine with 32 processors, and one that can perform spin-polarized self-interaction corrected density functional calculations. We are implementing several functions that will calculate, from the band structure, the Seebeck coefficient and the electrical conductivity.

So far we have calculated the properties of a few compounds. We found a great variation in their properties: $Si_{4\,6}$ is a wide band gap semiconductor, $Na_8\ Si_{46}$ is a doped Si_{46} with metallic character, $Na_8Al_{23}Si_{23}$ is a metal and $K_8\ Ge_{48}$ is a semiconductor and a good thermoelectric material. This variability gives us hope that we can find, among a hundred of such compounds and all their modification, a superior thermoelectric.